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Structure Determination of a New Trinuclear Iron Carboxylate, [Fe$_3$(μ^3-O)(HCOO)$_6$(γ-pic)$_3$]·(γ-pic)·(HCOO)

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Beamline(s): X3A1

Introduction: In the synthesis of a novel mixed-valence 2D layer complex [1], a by-product was observed to develop over time from the mother liquor. This by-product belongs to the class of basic trinuclear iron carboxylates, which we have been studying intensively [1,2]. It crystallizes in the rhombohedral space group R32 at room temperature with all three iron atoms crystallographically equivalent. A chemical test for Fe^{II} was negative. Crystals being of good quality made us attempt a low-temperature charge density study as an example of an oxidized trinuclear iron carboxylate compound.

Methods and Materials: A suitable single crystal (size: 0.13×0.11×0.10 mm^3) was cooled to 16(5) K using a liquid He-cooling device at beamline X3A1. 25696 reflections with (sinθ/λ)$_{max}$=1.00 Å^{-1} were collected with a Bruker SMART6000 CCD detector and integrated with SAINT+ with an internal agreement of R$_{int}$=0.037. The molecule remains in the space group R32 in the temperature range from room temperature to 16 K (a = b = 18.0128(3) Å, c = 10.4405(2) Å, α = β = 90°, γ = 120°; R(F)=0.040 for 4481 observed reflections (F$_o$>4σ(F$_o$)) and 87 parameters).

Results: At 16 K, the trinuclear iron carboxylate molecule lies with a crystallographic three-fold axis through the central O(1), see Figure 1. The Fe-O(1) distance is 1.9199(2) Å, which is longer than the average Fe-O(1) bond length (1.909(2) Å) in the valence trapped state of the related mixed-valence compound [Fe$_3$O(HCOO)$_6$(γ-pic)$_3$]·1.2γ-pic [1], as well as it is longer than average Fe-O(1) bonds in other oxidized trinuclear complexes. Furthermore, the Fe-N bond to the γ-pic ligand (2.161(1) Å) is significantly shorter than other reported Fe-N bonds to this ligand [1], even for divalent Fe. An explanation for the somewhat surprising bond lengths are sought in the charge density analysis.
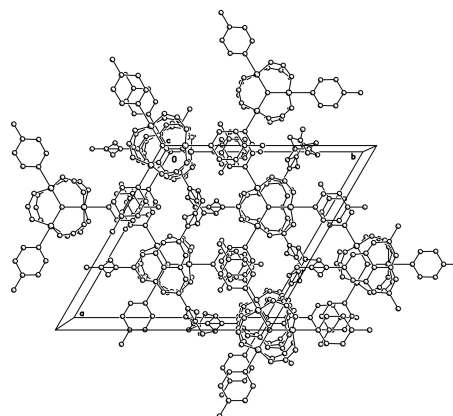
References:
[1] J. Overgaard, Ph. D. thesis, Department of Chemistry, University of Aarhus, Denmark, 2001.
[2] C. Wilson, *et al.*, *J. Am. Chem. Soc.* (2000), *122*, 11370-11379.
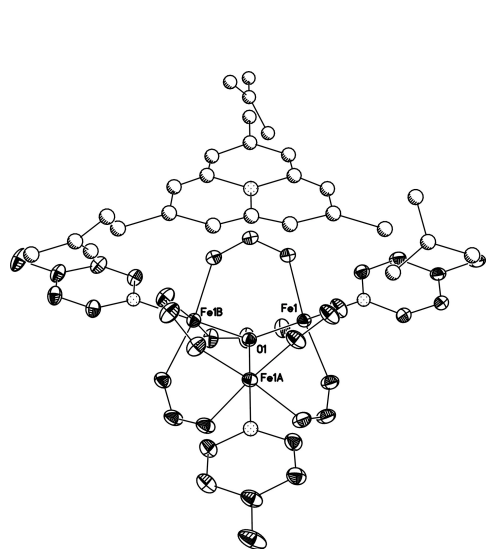
Figure 1. Thermal ellipsoids plot of **1** truncated at 50% probability levels.

Figure 2. Packing plot of **1**.